COATINGS. ENAMELS

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A LOW-BORON DIELECTRIC COATING FOR ALUMINUM

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A titanium-boron-silicate system containing alkali metal oxides and lead, strontium, cadmium, chromium, and cobalt oxides is studied for the purpose of developing a low-melting enamel coating for aluminum. The influence of the polyalkali effect and the $SiO_2 : TiO_2$ ratio on the conductivity and chemical resistance of the glass is studied. The possibility of obtaining a low-melting (firing temperature 540 – 560°C) corrosion-resistant enamel with a high resistivity based on the indicated glass system is demonstrated.

The firing temperature suitable for enameling aluminum is around 560°C. In this connection, low-melting enamels are needed (with a softening temperature $t_g = 450 – 500°C$). Such enamels can be based on alkali-silicate systems and alkali-silicate systems with additives of boron, lead, titanium, barium, calcium, zinc, antimony, and vanadium oxides. Certain fluorides, for instance, sodium and calcium fluorides, can be used. Usually, an attempt is made to keep the boron oxide content quite low, and sometimes this oxide is totally eliminated, since, like fluorides, it can degrade the chemical resistance of the enamel. Low-melting enamels based on phosphoric anhydride are used as well (USSR Inventor's Certif. Nos. 1057451 and 1470689) [1, 2]. Phosphate enamels are quite low-melting ($t_g = 400 – 500°C$) and have sufficient chemical resistance, but their dielectric properties are not always satisfactory.

To provide a low melting point, increased chemical resistance, and a high specific resistance, interest the $SiO_2 – B_2O_3 – TiO_2 – MO – M_2O$ system (where MO is PbO, SrO, CdO; M_2O is Li_2O, Na_2O, K_2O) is of special interest. The glasses of this system have good adhesion to aluminum and sufficient chemical stability, and their TCLE is $(130 – 135) \times 10^{-7}\ K^{-1}$. The TCLE of the glasses was determined within the temperature interval of 20 – 400°C at a heating rate of 2 K/min using a DKV-5A dilatometer, the chemical resistance of the glasses was determined by the granular method in accordance with GOST 10134.1–82, that of the coatings was determined by the "spot" breakdrown method according to ASTM C 282–53 [1, 2], and the volume resistivity at a temperature of 20 – 300°C was determined employing an E6–10 ohmmeter.

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The melting point of the aluminum substrate is 660°C. In order to prevent its warping, the coating has to be deposited at a temperature not exceeding 600°C.

Most glasses contain alkali metal oxides, which have a positive effect on the technological properties; however the chemical stability and electrical resistance of such glasses are not sufficiently high. It is known that the resistivity can be increased by using the polyalkali effect and by introducing alkali-earth metal oxides. [3]. At the same time, it is necessary to provide a specific-resistance level not lower than $10^{17}\ \Omega \cdot cm$ at a temperature of 20 – 100°C and a breakdown voltage of at least 2000 V.

Separate introduction of each alkali oxide decreases the glass melting temperature and increases its conductivity, but the intensity can be different. The resistivity decreased least of all upon introducing sodium oxide. Thus, at a temperature of 300°C, the specific resistance ρ_{300} of the systems below amounted to:

System	Specific resistance, $\Omega \cdot cm$
$0.8(SiO_2 – TiO_2) \cdot 0.2Li_2O$	8.9×10^5
$0.8(SiO_2 – TiO_2) \cdot 0.2Na_2O$	2.3×10^4
$0.8(SiO_2 – TiO_2) \cdot 0.2K_2O$	6.7×10^4

The presence of 20% (hereafter the molar content is indicated) alkali oxides in the glass composition makes it possible to obtain a low-melting glass ($t_g = 480°C$), which, however, has a low specific resistance ($10^4 – 10^5\ \Omega \cdot cm$ at a temperature of 300°C). Therefore, the aim was to reduce the total content of alkali oxides and study the effect of each alkali oxide and combinations of them on the properties of the glass and the enamel.

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Lithium oxide increases such important parameters of enamel as spreadability and uniformity of the coating thickness to a greater extent than sodium and potassium oxides. The chemical resistance of lithium and potassium enamel is classified as grade B, and of sodium enamel as grade C. With the aim of increasing the resistivity and chemical resistance of the glass, boron, lead, cadmium, and strontium oxides were introduced into the glass composition. The proportion between Li_2O, Na_2O, and K_2O was varied as well, while the content of boron oxide and oxides of the MO group in the system remained constant. The enamel firing temperature (glasses of the $SiO_2 – B_2O_3 – TiO_2 – M_2O – MO$ system) was varied within the limits of 540 – 560°C.

Partial replacement of Li_2O by Na_2O ($Li_2O : Na_2O : K_2O$ = 9 : 1 : 0) leads to an increase in ρ_{300}, namely, $10^8 – 10^9\ \Omega \cdot$ cm. Further modification of this proportion to 7 : 3 : 0 makes the specific resistance even higher: $10^{12} – 10^{13}\ \Omega \cdot$ cm. Upon introducing a third alkali oxide (K_2O), the resistivity continues to increase (this is presumably due to the polyalkali effect) [1, 3]. With the ratio $Li_2O : Na_2O : K_2O$ equal to 5 : 1 : 2.5, the glass obtained has $\rho_{300} = 10^{17}\ \Omega \cdot$ cm, a TCLE of $125.0 \times 10^{-7}\ K^{-1}$, and $t_g = 480$°C, the chemical resistance to 4% acetic acid is 0.27% loss of grain weight, and the chemical resistance of the coating is grade AA.

The effect of the ratio $SiO_2 : TiO_2$ on the properties of the glasses at a constant content of B_2O_3 and oxides of the groups MO and M_2O was studied as well (Fig. 1). With a decreasing $SiO_2 : TiO_2$ ratio, in general an S-shaped change is observed in the firing temperature and other properties of the enamel. True, the curves exhibit smoothed maxima and minima, whose presence is presumably due to different amounts of a crystalline phase that appears in enamel firing. According to data of an x-ray phase analysis, TiO_2 in the form of anatase is the crystalline phase.

The best chemical resistance was shown by glass containing 12.5% TiO_2. With a higher or lower content of TiO_2, the chemical resistance decreases. No perceptible effect of the $SiO_2 : TiO_2$ ratio on the electrical properties of the glass was established.

Introduction of PbO, SrO, CdO into the glass composition increases the chemical resistance of the glass and the enamel, and in the presence of a substantial amount of alkali oxides (a total content of up to 15%) it even leads to decreased conductivity of the glass (the suppression effect) [3].

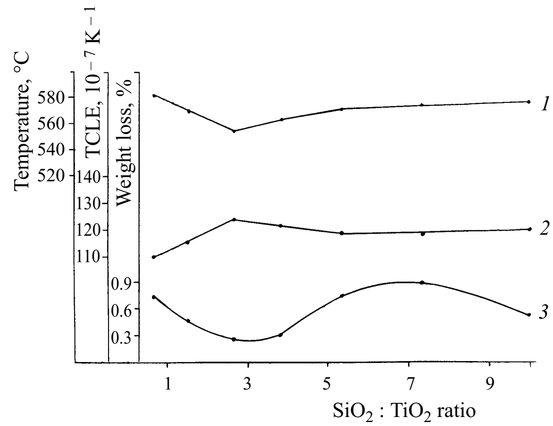

Fig. 1. Change in the properties of glasses and enamels of the titanium-boron-silicate system as a function of the $SiO_2 : TiO_2$ ratio: *1*) enamel firing temperature; *2*) TCLE; *3*) chemical resistance to 4% acetic acid.

Glasses in which the total content of alkali oxides constitutes up to 12% have a TCLE of (120 – 125) $\times 10^{-7}\ K^{-1}$. Introduction of adhesive oxides, namely, Co_3O_4, Cr_2O_3 (up to 1% above 100%), compensates to a significant degree for this drawback. The adhesion of the enamel to the substrate is 100 – 110 kg/cm^2, and 12 cycles of 470 – 20°C do not impair the adhesion.

A decrease in the alkali oxide content, the presence of TiO_2 in the glass composition (in an amount equal to or slightly higher than the alkali oxide content), and partial replacement of K_2O and Na_2O by Li_2O result in increased chemical resistance of the glasses and enamels based on them, along with good dielectric parameters.

Thus, the proposed glass composition ($Si_2O – B_2O_3 – TiO_2 – PbO – SrO – CdO – Li_2O – Na_2O – K_2O – Co_3O_4 – Cr_2O_3$) can be regarded as a base composition for the development of enamel coatings for aluminum plates.

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